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Experimental Protocol for Determining Ozone Reaction Rate Constants

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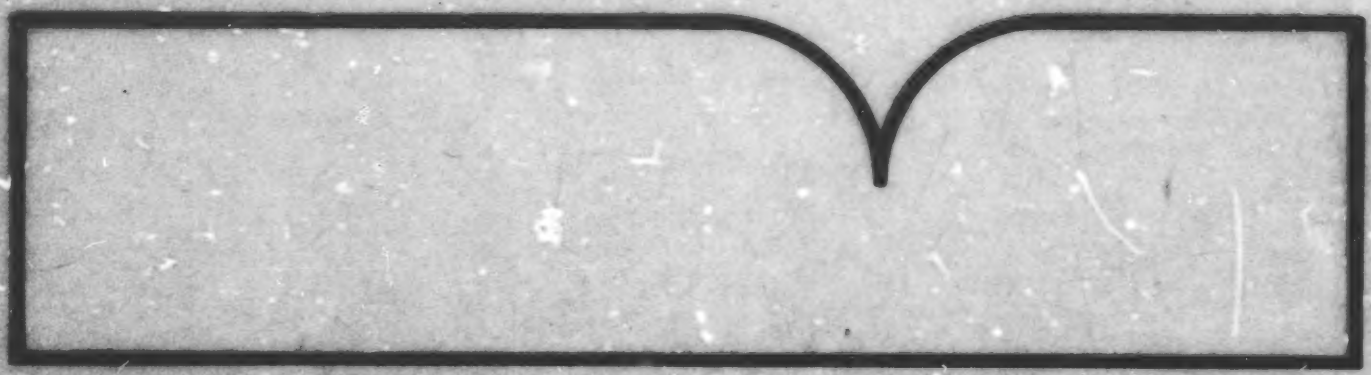

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An experimental protocol for the determination of room temperature rate constants for the reactions of ozone (O_3) with chemicals in the gas phase has been developed and is described in detail. This protocol will thus provide a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e. attack by ozone) of organic substances which may be emitted into the environment. The experimental technique is based upon monitoring the decay of ozone (initially present at approximately 1 ppm) in the presence and absence of known excess concentrations of the test compound, with pure air as a diluent gas. The ozone reaction rate constants are then calculated from the dependence of the observed ozone decay rates on the concentration of the test compound. The reactions are carried out in approximately 150-180 liter Teflon reaction bags. The reaction bag is initially divided into two approximately equal sub-chambers. Known concentrations of ozone and the test compound are then introduced into the two sub-chambers, ozone into one, and the test compound into the other. The barrier between the two sub-chambers is then removed, the contents of the reaction bag mixed, and the ozone concentration monitored as a function of time. Using this technique, ozone rate constants 10^{-20} cm^3 $molecule^{-1}$ sec^{-1} can be readily measured for test compound concentrations of approximately 0.1 torr (i.e. 100 ppm), which encompasses the reactivities of interest from an atmospheric point of view.

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EXPERIMENTAL PROTOCOL FOR DETERMINING OZONE REACTION RATE CONSTANTS

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ABSTRACT

An experimental protocol for the determination of room temperature rate constants for the reactions of ozone (O_3) with chemicals in the gas phase has been developed and is described in detail. This protocol will thus provide a basis for evaluating the relative importance of one atmospheric reaction pathway (i.e. attack by ozone) of organic substances which may be emitted into the environment.

The experimental technique is based upon monitoring the decay of ozone (initially present at ~1 ppm) in the presence and absence of known excess concentrations of the test compound, with pure air as a diluent gas. The ozone reaction rate constants are then calculated from the dependence of the observed ozone decay rates on the concentration of the test compound. The reactions are carried out in ~150-180 liter Teflon reaction bags. The reaction bag is initially divided into two approximately equal sub-chambers. Known concentrations of ozone and the test compound are then introduced into the two sub-chambers, ozone into one, and the test compound into the other. The barrier between the two sub-chambers is then removed, the contents of the reaction bag mixed, and the ozone concentration monitored as a function of time. Using this technique, ozone rate constants $\geq 10^{-20}$ cm^3 $molecule^{-1}$ sec^{-1} can be readily measured for test compound concentrations of ~0.1 torr (i.e. 100 ppm), which encompasses the reactivities of interest from an atmospheric point of view.

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TABLE

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SECTION 1

INTRODUCTION AND BACKGROUND

Chemical compounds emitted into the atmosphere are removed or degraded by several pathways, these being chemical gas phase reactions or wet or dry deposition. Laboratory and environmental chamber studies have shown that for the ambient atmosphere the following gas phase removal routes are likely to be important (see, for example, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Atkinson et al. 1979, Atkinson and Lloyd 1980, and references therein):

- Photolysis, which involves absorption of light followed by isomerization or decomposition
- Reaction with ozone (O_3)
- Reaction with the hydroxyl (OH) radical
- For aromatic compounds containing an -OH substituent group, reaction with the nitrate (NO_3) radical.

Hence, in order to assess (a) the atmospheric lifetime of compounds with respect to these gas-phase removal processes and (b) the relative importance of each of these reaction pathways, rate constants for photolysis and/or chemical reaction must be experimentally determined for individual compounds.

The experimental procedure detailed in this protocol is designed to enable rate constants for reaction with O_3 to be determined at room temperature.

In the atmosphere, where the reaction

$$O_3 + \text{chemical} \rightarrow \text{products}$$

occurs, the decay of the chemical via this reaction is given by

$$-d[\text{chemical}]/dt = k^{O_3}[O_3][\text{chemical}] \quad (1)$$

where [ ] denotes concentration and k^{O_3} is the rate constant for reaction of O_3 with the particular chemical. Since the O_3 concentration remains constant or approximately so in the ambient atmosphere, equation (1) may be rearranged to yield

$$-d\ln[\text{chemical}]/dt = k^{O_3}[O_3] \tag{2}$$

and

$$\ln([\text{chemical}]_{t_o}/[\text{chemical}]_t) = k^{O_3}[O_3](t-t_o) \tag{3}$$

where $[\text{chemical}]_{t_o}$ and $[\text{chemical}]_t$ are the concentrations of the chemical at times t_o and t, and ln is the logarithm to the base e. Thus under atmospheric conditions, the 1/e lifetime, τ, (i.e., the time for the concentration of the chemical due to reaction with O_3 to decrease by a factor of e = 2.7) of any chemical with respect to reaction with O_3 is given by

$$\tau = (k^{O_3}[O_3])^{-1} \tag{4}$$

where $[O_3]$ is the ambient atmospheric concentration (both k^{O_3} and $[O_3]$ must be in compatible units, i.e., cm^3 $molecule^{-1}$ sec^{-1}, liter $mole^{-1}$ sec^{-1} or ppm^{-1} min^{-1} units for k^{O_3}, and molecule cm^{-3}, mole $liter^{-1}$ or ppm units, respectively, for $[O_3]$).

For a typical lower troposphere ozone concentration of 40 ppb (Singh et al., 1978), the rate constants which yield 1/e lifetimes of one hour, one day, one week, one month, and one year are given in Table 1 for the three sets of most commonly used units.

The experimental approach described below is based upon observing the increased rate of ozone decay in the presence of a large excess of the test compound. Thus the two processes removing O_3 in the presence of the test compound are:

O_3 + test compound	→ products	with a rate constant k^{O_3}
O_3	→ wall	with a rate constant k_w

TABLE 1. RATE CONSTANTS FOR REACTION WITH O_3 WHICH YIELD SELECTED 1/e LIFETIMES IN THE PRESENCE OF 40 PPB OF O_3

1/e Lifetime	Rate Constant*		
	ppm^{-1} min^{-1}	liter $mole^{-1}$ sec^{-1}	cm^3 $molecule^{-1}$ sec^{-1}
1 hour	4.1×10^{-1}	1.7×10^{5}	2.8×10^{-16}
1 day	1.7×10^{-2}	7.0×10^{3}	1.2×10^{-17}
1 week	2.5×10^{-3}	1.0×10^{3}	1.7×10^{-18}
1 month	5.7×10^{-4}	2.3×10^{2}	3.9×10^{-19}
1 year	4.7×10^{-5}	1.9×10^{1}	3.2×10^{-20}

*At 298°K and 760 torr.

and hence

$$-d[O_3]/dt = (k_w + k^{O_3}[\text{test compound}])\ [O_3] \qquad (5)$$

With the concentration of the test compound being much in excess of the initial ozone concentration ($[\text{test compound}]/[O_3]_{initial} > 10$), the test compound concentration remains essentially constant throughout the reaction, and equation (5) may be rearranged to yield:

$$-d\ln[O_3]/dt = k_w + k^{O_3}\ [\text{test compound}] \qquad (6)$$

Hence with a knowledge of the background ozone decay rate in the absence of added compound, k_w, and the ozone decay rates, $-d\ln[O_3]/dt$, at known concentrations of the test compound, k^{O_3} may be readily determined. Since it is difficult to detect incremental changes in the ozone decay rates that are much smaller than k_w, lower limits of the rate constants that can be determined occurs when $k^{O_3}[\text{test compound}] \simeq k_w$, while the upper limit is determined by the response time of the ozone monitoring device.

SECTION 2

GENERAL EQUIPMENT AND MATERIALS REQUIRED

To determine rate constants for the reaction of ozone with compounds using the method outlined above, the following major equipment is needed:

- An ozone monitor equipped with a filter to remove particulates which could cause an interfering response
- An ozone generator
- A Teflon bag or chamber in which the reaction can be carried out
- A calibrated rotameter or other calibrated flowmeter which covers the flow range of 1 to 10 liter min^{-1}

The specific requirements and recommendations for these items of equipment are discussed below.

A. Ozone Monitor

A chemiluminescence ozone analyzer is recommended for this protocol since the ozone analyzers utilizing ultraviolet absorption tend to respond not only to ozone but also to some chemicals which absorb radiation at 253.7 nm (e.g., the cresols [Atkinson et al. 1980]). This may include some of the ozonolysis reaction products. These interferences can, depending on whether the reactant or the ozonolysis products cause the interference, give rise to too rapid or too slow an observed ozone decay. In view of these potential problems, it is desirable to use a chemiluminescence O_3 monitor which utilizes the emission arising from the ozone-ethene reaction. The ozone analyzer used will have an optimum sampling rate specified by the manufacturer and any accurately monitored sampling rate less than 2 liter min^{-1} is acceptable.

The ozone analyzer should be calibrated according to the manufacturer's specifications.

B. Ozone Generator

There are two types of ozone generators commercially available, one using a "silent" electrical discharge to yield 1-5% ozone in air or O_2, the other using ultraviolet photolysis of air or O_2 in a quartz tube to generate of the order of 1 ppm O_3. Both types operate at useful flow rates of 1-5 liter min^{-1}. Since use of the latter type of ozonizer, i.e., those yielding ppm concentrations of ozone, results in an inordinately long fill time of the reaction bag, the use of an ozone generator capable of yielding 1-5% ozone in air or O_2 (e.g., a Welsbach T-408 ozone generator or equivalent) is recommended. Dilution of this high O_3 concentration to ppm concentrations in the reaction system can be readily and rapidly carried out, as discussed below in Section 3.

The approximate percentage ozone output of the generator can be readily determined by injecting a known volume, V_1, of the O_3/O_2 or O_3/air mixture into a known volume V_2 of pure air in the reaction bag and monitoring the O_3 concentration. The percent O_3 in the generator output is given by

$$\% O_3 = 10^{-4}[O_3] \times V_2/V_1$$

where $[O_3]$ is the observed O_3 concentration in ppm and V_1 and V_2 are in the same units, i.e., liters or milliliters. This determination also serves to ozone condition the reaction bag and the Teflon sampling lines. For the reaction bag recommended here, V_2 ~ 150-180 liters, and with a typical ozone generator, a volume V_1 of ~20 ml should be used.

C. Reaction Chamber and Sampling Ports

1. Reaction Chamber

A simple, yet totally appropriate, reaction chamber can be made by folding in half (lengthwise) a 185 $\pm$ 10 cm long, 140 $\pm$ 7 cm wide piece of 2 mil thick FEP Teflon (FEP Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.). This yields a pillow-shaped bag with final dimensions of ~185 cm x 70 cm, and a volume of ~150-180 liters, which is an optimum size for the protocol described here. Teflon is the preferred material for construction of the reaction chamber because of its general inertness to ozone and its lack of hydrocarbon offgassing.

2. Injection and Sampling Ports

Prior to heat sealing the Teflon chamber sides, ports for injection of ozone and the test compound, and for ozone sampling, must be fitted. These sampling and injection ports should be constructed of TFE Teflon (TFE Teflon is a registered trade name of E. I. du Pont de Nemours and Co., Inc.) nuts and bolts with the appropriate pipe-to-Swagelok (Swagelok is a registered trade name of Crawford Fitting Company) stainless steel fittings to connect to 1/4" o.d. Teflon tubing.

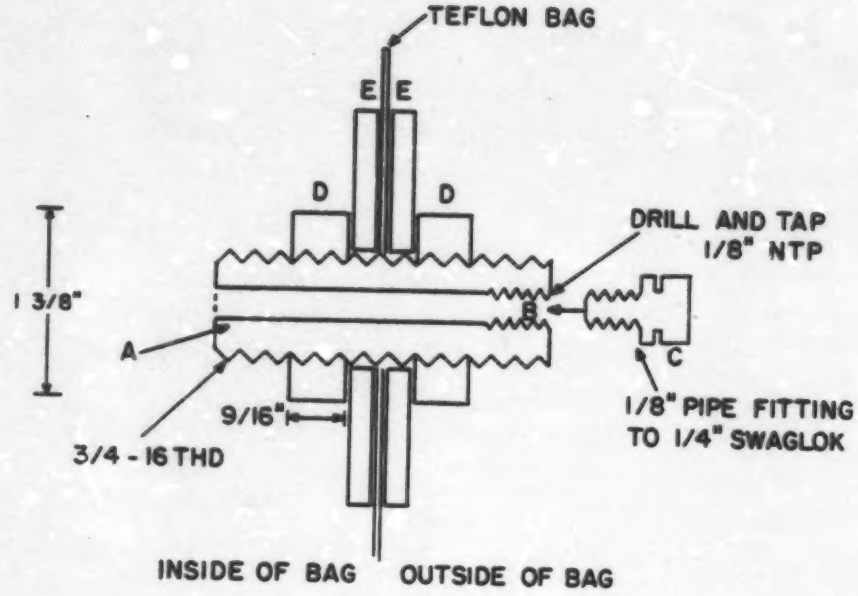
Figure 1 shows the design of the sampling and injection ports used in developing this protocol. Each port consists of a 3-4" long hollow bolt of Teflon (A), machined on the interior and exterior surfaces with threads. The interior screw threads (B) fit a 1/8" pipe to 1/4" Swagelok fitting (C), and only need to be on the part of the bolt extending on the outside of the bag. Two Teflon nuts (D) then screw over the bolt (A), one on the inside of the bag, the other on the outside. Large Teflon washers (E) are placed between the Teflon bag and the nuts (D), thus enabling the nuts to be tightened without twisting or stretching the Teflon bag. The ports can then be capped with stainless steel Swagelok caps.

Whenever removing or replacing sampling lines, or capping ports, two wrenches should be used to avoid overstressing the Teflon ports since the threaded bolts are thin in places and easily broken.

One side of the bag should have one port and the other may have one or two as shown in Figure 2. For the injections a three-way stainless steel Becton-Dickinson (BD) valve, adapted through Swagelok fittings and Teflon tubing (Figure 3) to attach to the sampling port on the reaction bag, may be used satisfactorily.

3. Heat Sealing

The Teflon ports are first assembled on the side of the chamber with the fold by tightening the Teflon nuts, as detailed above and as shown in Figures 1 and 2. The holes in the Teflon sheet through which the Teflon bolts (A) fit can be conveniently made using a cork borer. The sides of the resulting "pillow-shaped" bag are sealed together with a 500 watt thermal impulse heat sealer with a 12" long heating surface. It will probably be necessary to carry out preliminary testing of this



A HOLLOW TEFLON BOLT
B INTERIOR SCREW THREADS TO FIT 1/8" PIPE FITTING
C 1/8" PIPE TO 1/4" SWAGLOK FITTING
D TEFLON NUTS
E TEFLON WASHERS

Figure 1. Injection and sampling ports.

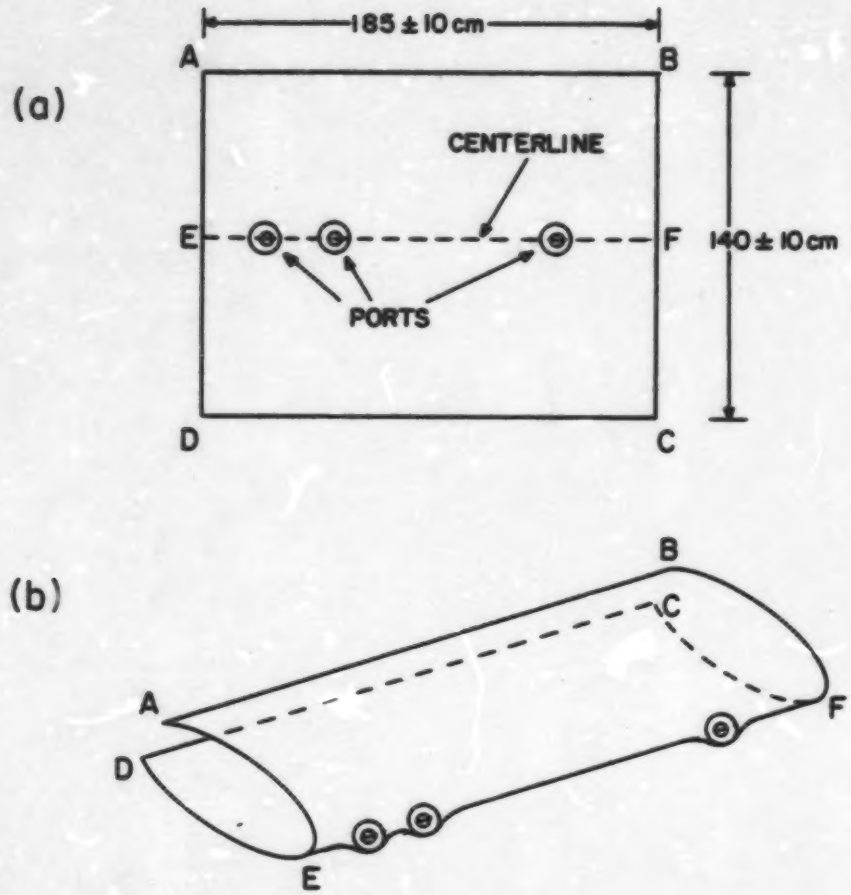


Figure 2. Construction of the Teflon reaction bag.

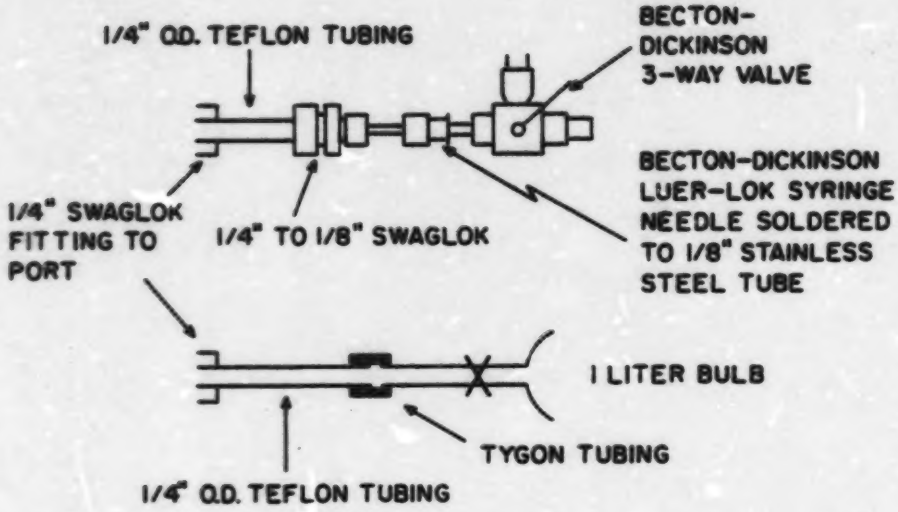


Figure 3. Gas and liquid injection systems.

heat sealing technique using scrap pieces of Teflon to obtain a heat setting that yields a strong seal.

D. Metal Rods

In the experiments to determine ozone decay rates the Teflon chamber is divided into two sides, or subchambers, using three solid metal rods, as discussed in section 3B.1 below. These rods must be ~20 cm longer than the width of the chamber in order for them to be supported by clamps. A suitable rod diameter is ~1 cm, although this dimension is not critical.

E. Reaction Bag Cover

An opaque cover is necessary in order to avoid illumination of the chamber and hence possible photolysis of the ozone or the test compound being studied. A large opaque plastic sheet functions well.

F. Seal Reinforcement and Leak Testing

The heat sealed sides can be further protected from leaks by covering the heat-sealed seams with green Mylar tape. After the bag is constructed it should be tested for obvious leakage by filling the entire undivided bag with pure air (ultra-high purity) to capacity (not excessively so as to split the seams) and then allowing the inflated bag, with all ports capped, to sit for one or two hours. After this period of time, the amount of deflation can be visually estimated. A certain amount of air will have permeated through the Teflon, but the bag should still be largely filled, and no obvious leaks should result from applying a small amount of pressure to the bag. The seams should be carefully examined for splits or tears, and, if any holes are found, they should be resealed (probably at a lower heat setting) and more Mylar tape applied to reinforce the seams.

G. Flowmeter

1. Range and Application

A rotameter (Matheson 604 flowmeter or its equivalent) with a flow range of ~1 to 10 liter min^{-1} is an effective means for controlling and monitoring the rate of fill of the reaction chamber. In order to calculate the volume of air in the chamber the flow rate used to fill the two individual sides must be known. When not flushing a test compound into the chamber, the fill rate may be relatively rapid, i.e., ~7-10 liter min^{-1}.

However, when a liquid needs to be introduced into the chamber, this is accomplished by flushing an ~1 liter bulb containing the compound of interest with pure air into the bag at a lower flow rate, i.e., ~3 liter min^{-1} (at high flow rates the test compound may not fully vaporize before the bag is filled). A slower flow rate still may be useful for particularly nonvolatile compounds, though use of a heat gun will aid vaporization in these cases.

2. Calibration of the Rotameter

Rotameters are often accompanied by a manufacturers calibration curve for air. Although this calibration curve, if available, could be used, it is advisable to accurately determine the flow rate calibration curve. Flow rates should be determined at several (at least five) rotameter settings covering the flow rates to be used (i.e., 1-10 liter min^{-1}). At these flow rates a wet test meter (Precision Scientific Model No. 63126 or equivalent) is preferable for measuring the flow rates, although a 1000 cm^3 or (preferably) a 2000 cm^3 bubble flowmeter can also be used. If neither a wet test meter nor a bubble flowmeter is available, a bubble flowmeter can be readily constructed by narrowing one end of a large glass tube (~5 cm diameter), as shown in Figure 4. Indelible lines can be drawn on the glass at intervals of 100 cm^3 upon adding water from a 100 cm^3 volumetric flask which has been filled to the mark and noting the water level after each successive addition of water (with, as shown in Figure 4, the zero line being above the narrow portion of the flowmeter) with the flowmeter in a vertical position. To the narrow end of the glass tube a glass "T" is attached by Tygon tubing, and the lower arm is enclosed with a disposable pipette bulb. To the other arm of the "T" a Tygon tubing line which carries the gas is attached.

The pure air should first be sent through the rotameter and its setting adjusted and noted. When using a wet test meter, measure the time, t, for a change of volume, V. For a bubble flowmeter, first squeeze the pipette bulb (containing soap solution, e.g., SNOOP [a registered trade name of Nupro Company]) to start a soap bubble and again measure the time, t, for the soap bubble to pass through a known volume V (the sidewalls of the bubble flowmeter should be well washed with soap solution so that

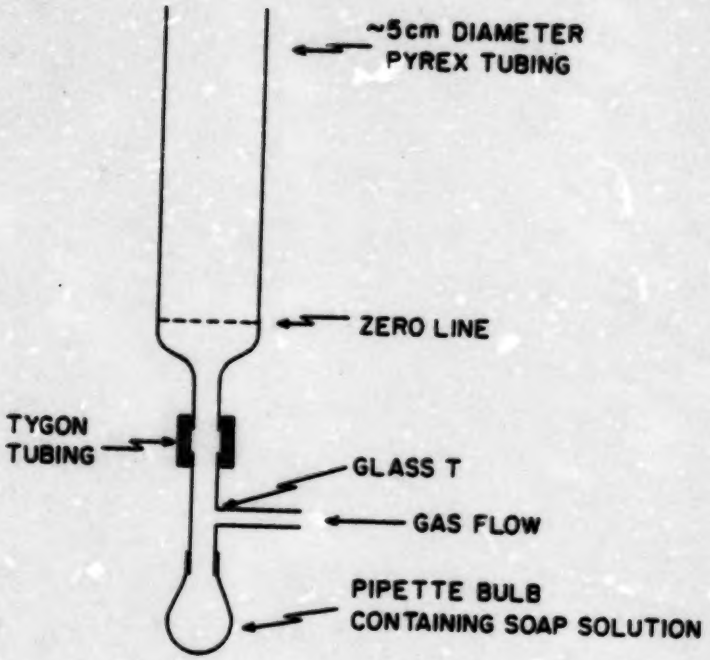


Figure 4. Design of a bubble flowmeter.

bubbles will not break). For both types of flowmeters at least three repeat readings should be taken at each rotameter setting. The volumes V should be such that the corresponding times t exceed 10 seconds. The flow rate F (in liter min^{-1}) is given by

$$F = \frac{V(cm^3) \times 60}{t(sec) \times 1000}$$

SECTION 3

EXPERIMENTAL PROTOCOL

A. Determination of the Background Disappearance Rate, k_w, of Ozone

Before any rate constants for the reactions of O_3 with the test compound(s) can be determined, the background ozone decay rate, k_w, must first be determined. Additional measurements of the background ozone decay rate should be made periodically during a series of rate constant determinations, preferably after every third or fourth experiment. The experimental procedure for determining k_w is as follows:

1. Pure Air Fill

For all rate constant determinations (including those of the background ozone decay rate k_w) pure air is used as the diluent or matrix gas. If ultra-high purity nitrogen or argon is used as the diluent gas, erroneously high O_3 decay rates and rate constants may result from the occurrence of secondary reactions (see, for example, Japar et al. 1976), which are minimized by the presence of O_2. A commercial cylinder of Ultra High Purity air is recommended. The pure air flow rate into the reaction bag in the single, i.e., undivided, mode should be controlled with the calibrated rotameter and, from the time required to fill the bag, the volume of the bag can readily be calculated [Volume V = (flow rate) x (time)].

2. Injection of O_3

After the pure air fill the bag should be covered with the opaque plastic sheet to avoid O_3 photolysis, and ~20 cm^3 of approximately 1% O_3 in oxygen (or air) in a 100 cm^3 all-glass gas syringe (Becton-Dickinson Yale with glass Luer tip) is then injected into the bag. Prior testing of the ozonizer output (Section 2B) and a knowledge of the bag size is of course necessary in order to obtain the correct volume of O_3 in O_2, or air, to be injected into the bag. An initial ozone concentration of ~1 ppm is recommended. The bag should be mixed for 1-2 minutes by alternately pushing opposite sides of the bag down.

3. Ozone Measurement

Before beginning ozone monitoring in the bag, the ozone analyzer should be allowed to warm up according to the manufacturer's specifications. When the ozone monitor is warmed up, sampling from the reaction bag may begin. Teflon sampling lines (1/4 in. o.d.) should be used between the bag and the ozone monitor in order to avoid losses experienced with, for example, Tygon or nylon tubing. These sampling lines should be conditioned when first installed by sampling for ~1 hour from the reaction bag containing ~1 ppm of O_3 (Section 2B). The first 3-5 minutes sampling should be neglected since initial flushing of the sample lines is needed. The ozone concentration, $[O_3]$, should then be monitored for a minimum of one hour, and preferably for ~3 hours. The ozone concentrations, as monitored by the ozone analyzer, can be recorded either on a stripchart recorder connected to the analyzer output (as shown in Figure 5) or by recording manually the instruments digital or meter readout. The stripchart recorder or the ozone monitor meter should be correctly zeroed and spanned.

4. Data Analysis

Analysis of the data involves listing the $[O_3]$ values (taken from the stripchart recorder or as recorded manually) and the times at which they were measured.

The O_3 wall decay is defined by:

$$-d[O_3]/dt = k_w[O_3] \tag{7}$$

or

$$-d\ln[O_3]/dt = k_w \tag{8}$$

Integration of equation 8 yields:

$$\ln([O_3]_{t_o}/[O_3]_t) = k_w(t-t_o) \tag{9}$$

where $[O_3]_{t_o}$ and $[O_3]_t$ are the ozone concentrations at times t_o and t, respectively. The time t_o is chosen to be the time of the first ozone reading after the 3-5 minute sample line flush-out period. Hence a plot of

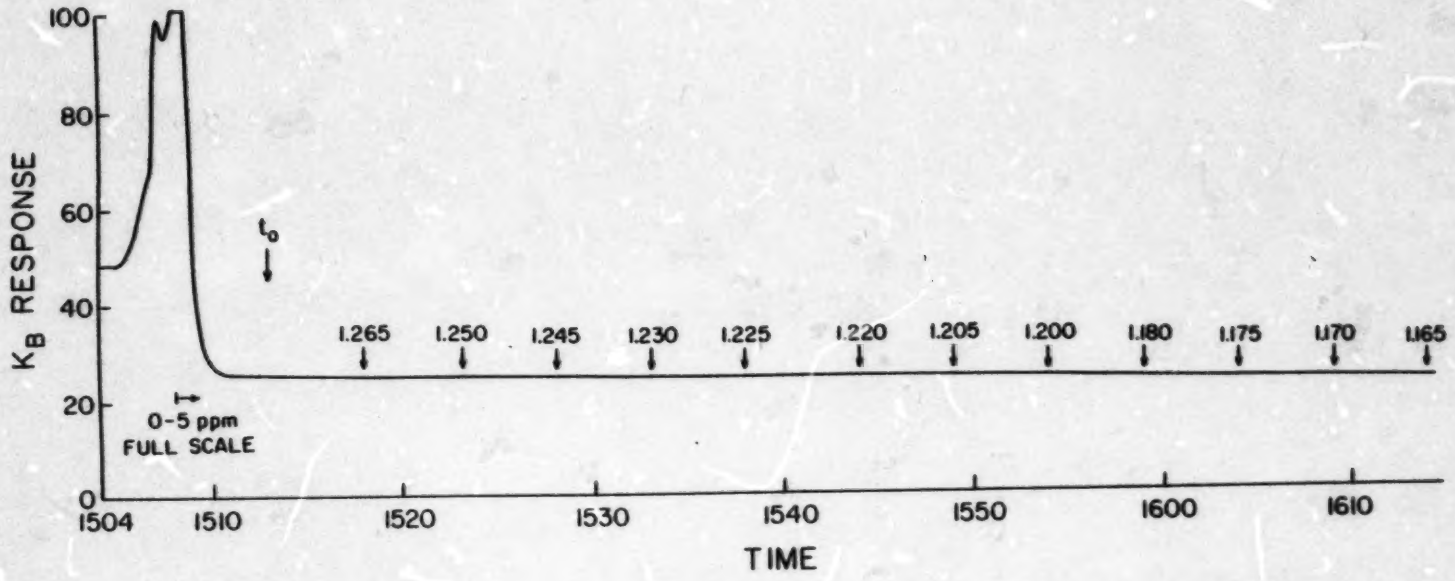


Figure 5. Background ozone decay as monitored on a stripchart recorder.

$\ln([O_3]_{t_o}/[O_3]_t)$ against $(t-t_o)$ (in minutes) should yield a straight line of slope k_w, as shown in Figure 6 for the data of Figure 5. At least 10 data points at equally spaced times t should be obtained and plotted. The slope of this plot is then obtained by least squares analysis.

Typically, values of k_w ~0.001 min^{-1} (corresponding to an ozone half-life of ~12 hours) have been obtained for Teflon reaction bags of the type described in this protocol. For practical purposes, values of k_w < 0.01 min^{-1} are necessary. If values of k_w < 0.01 min^{-1} are not initially obtained, the reaction bag should be allowed to remain for $\gtrsim$ 12 hours with ~1 ppm of ozone in pure air in it in order to condition the bag. After such a conditioning, the bag should be emptied completely with a metal bellows pump and then refilled and emptied again several times, prior to repeating the determination of k_w. This conditioning treatment of the bag should be repeated until the background O_3 removal rate falls below 0.01 min^{-1}. As noted above, determinations of k_w should be carried out on a regular basis, i.e., every fourth or fifth experiment.

B. Experimental Procedure for the Determination of Rate Constants for Reaction with Ozone

1. Filling the Reaction Bag

Prior to each new experiment, the reaction bag should be completely emptied using a metal bellows pump whose exhaust is expelled into a hood. The bag should then be filled with pure air and pumped out again to remove any test compound or O_3 from the previous run.

The reaction bag is then divided into two sides by wrapping the bag around the metal rods as shown in Figure 7. The rods are firmly clamped together on the two ring stands. By marking the dividing point of the bag with tape, reproducible divisions of the bag can readily be achieved.

The sides of the divided bag will be called Side A and Side B for the purpose of the following discussion. In this protocol, Side A is the side in which the compound being tested is initially injected, and Side B is that side into which O_3 is initially injected.

After bag division, Side B is filled with pure air while monitoring the flow rate with the calibrated rotameter. Using a flow rate in the region of ~7-10 liter min^{-1}, the time required to fill the bag (i.e., visually filled but not excessively so as to cause undue stress on the seams) is

Time	Elapsed Time ($t-t_o$) min	$[O_3]$ppm	$\ln([O_3]_{t_o}/[O_3]_t)$
1513	0	1.270	0.0000
1518	5	1.265	0.0039
1523	10	1.250	0.0159
1528	15	1.245	0.0199
1533	20	1.230	0.0320
1538	25	1.225	0.0361
1543	30	1.220	0.0402
1548	35	1.205	0.0525
1553	40	1.200	0.0567
1558	45	1.180	0.0735
1603	50	1.175	0.0777
1608	55	1.170	0.0820
1613	60	1.165	0.0863

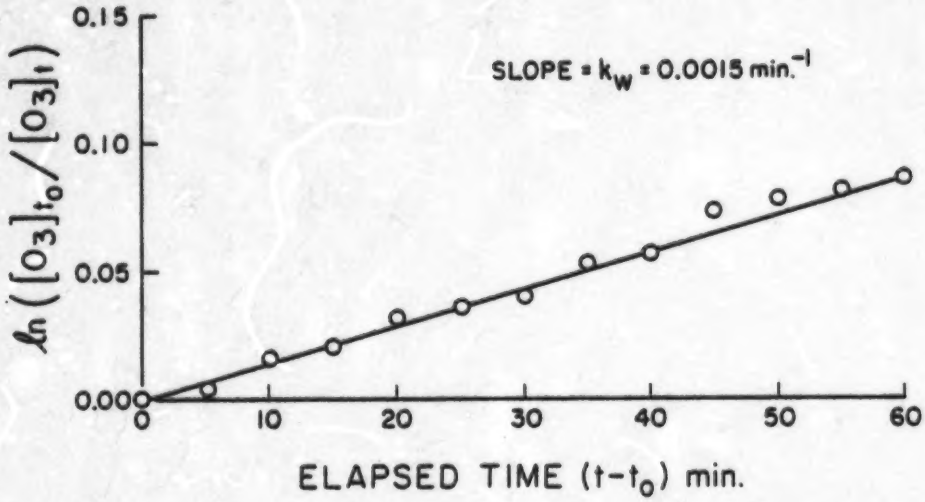


Figure 6. Plot of $\ln([O_3]_{t_o}/[O_3]_t)$ against $t-t_o$ for the background ozone decay data shown in Figure 5.

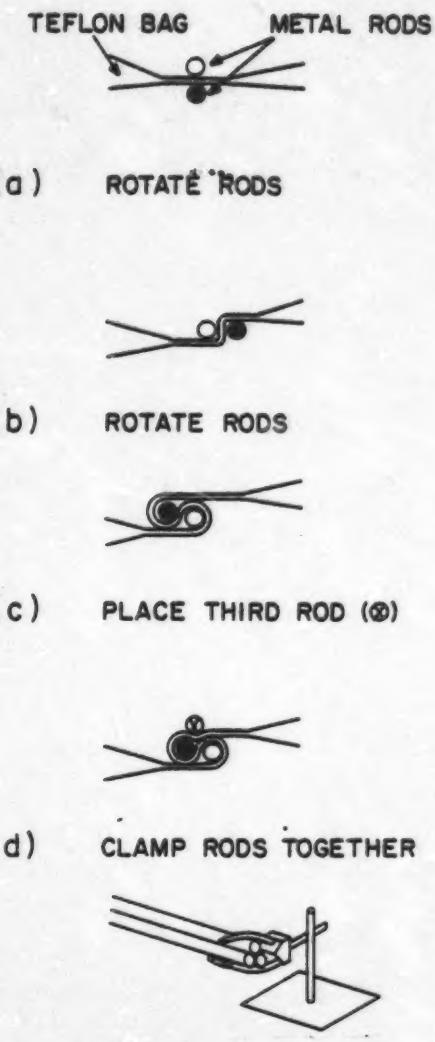


Figure 7. Division of the Teflon reaction bag into two sides using the solid metal rods.

noted. The volume of Side B, i.e., (flow rate) x (time required to fill), will be used in later calculations. The bag should be covered to avoid illumination.

2. Ozone Injection

Ozone is injected into Side B using an all-glass syringe as described in Section 3A.2. In order to ensure that pseudo-first-order kinetics apply, it is necessary to employ conditions such that the initial [test compound]/[O_3] ratio is $\geq$ 10, and hence a knowledge of the initial O_3 concentration in the undivided reaction bag (i.e., Side A + Side B), is necessary prior to introduction of the test compound into Side A. This requires either that the output of the ozonizer is reasonably accurately known, or that the ozone concentration in Side B of the divided bag can be briefly monitored using the ozone analyzer and, by dividing this concentraton by two, the O_3 concentration in the entire bag, (i.e., Sides A and B undivided) can be estimated. As in Section 3A (determination of background ozone decay rates), the desired initial O_3 in the entire bag, i.e., Sides A and B, is ~1 ppm.

3. Introduction of Test Compound

As has been discussed above, in order to operate under pseudo-first order kinetic conditions with the test compound in excess, the initial [test compound]/[O_3] ratio must be $\geq$ 10. Hence for an initial O_3 concentration of ~1 ppm, the test compound concentration in the entire reaction bag, i.e., Sides A and B, must be $\geq$ 10 ppm. Since the rate constant for reaction of the test compound with ozone is obviously not known, it is convenient to use an initial test compound concentration of ~10 ppm. If the ozone decay rate is slow, i.e., less than 3-5 times k_w, then, if possible, higher concentrations of the test organic must be used (low vapor pressures may preclude this). If the ozone decay is fast, i.e., with a half-life of a few minutes, then the initial test compound concentration (and the initial ozone concentration, to keep [test compound]/$[O_3]_{initial}$ ~10) must be reduced.

The following protocol details the introduction of a test compound to yield a concentration of ~10 ppm in the undivided bag.

a. Gaseous Compounds

If the compound to be tested is gaseous at room temperature, then it can be introduced directly into the already-filled Side A. As with the filling of Side B, the volume of Side A should be obtained from the flow rate and the fill time used.

The volume, V, of gaseous test compound needed is then given by:

$$V(cm^3) = 10^{-3} \times [\text{desired concentration (ppm)}] \times [\text{volume of entire bag, i.e., Sides A and B (liters)}] \quad (10)$$

Using the reaction bag described in this protocol, approximately 1.8 cm^3 of gas are required to yield a concentration of 10 ppm in the bag. With such a small volume of gas, the 1.8 ml of gas is first transferred from a 5 ml all-glass gas syringe into a 100 ml all-glass gas syringe containing ~98 ml of pure air. For this transfer the two syringes are connected tip-to-tip by an ~0.4 in. long Tygon tube, as shown in Figure 8.

The contents of the 100 cm^3 all-glass syringe are then injected into Side A of the bag through the Becton-Dickinson three-way valve, and the percentage of the test compound remaining in the injection valve is in this manner reduced.

b. Liquid Compound

If the test compound is a liquid, a different method of injection and of calculating the amount needed is necessary. For the reaction bag described in this protocol approximately 10 µl of liquid will give a concentration appropriate for an experiment aimed at an initial concentration of ~10 ppm, since for the liquid case:

$$V\ (\mu\text{liters}) = 10^{-4} \times [\text{desired concentration (ppm)}] \times \frac{[\text{Volume of bag (liters)}] \times \text{Molecular Weight (gm)}}{\text{Density (gm cm}^{-3}) \times 2.46} \quad (11)$$

at room temperature.

It is necessary that the test compound be of the highest purity possible, since any impurities may react with O_3 much faster than the actual test compou (thus, for example, the presence of alkene impurities in a

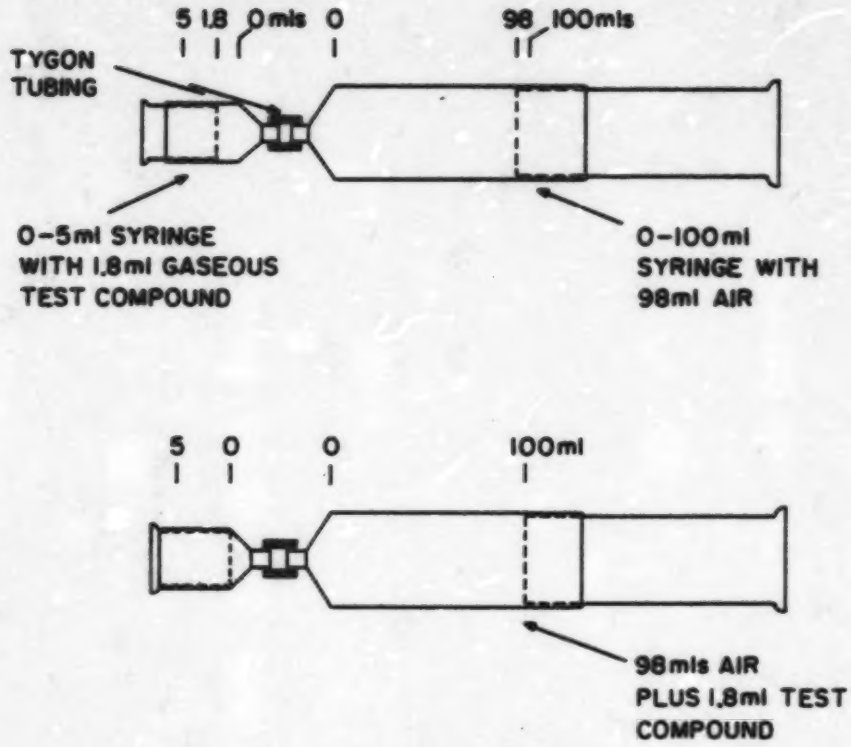


Figure 8. Syringe-to-syringe gas transfer.

saturated hydrocarbon would lead to an erroneously high rate constant, and atmospheric reactivity, ascribed to the saturated hydrocarbon). Hence, the purity of the test compound must be known, and the impurities quantitatively identified by, for example, gas chromatographic analysis.

Furthermore, any tendency of a compound to air oxidize or polymerize will lead to low volatility residues and hence errors when carrying out liquid injections. The compounds should, if such problems are known to be likely, be distilled by conventional means, i.e., vacuum distillation with liquid nitrogen trapping, vapor transfer from trap-to-trap at dry ice temperature, or by distillation at atmospheric or subatmospheric pressure.

Full safety precautions consistent with the known or unknown toxic, mutagenic or carcinogenic hazards of the test compounds must be taken, i.e., if the test compound is known to be hazardous or toxic, or if there is a reason to believe that it is, then handling should be carried out in a hood with disposable gloves, using a variable micropipette with disposable tips. Used gloves and tips should be disposed of according to safety regulations. If the toxicity of the compound is not a problem, a 10 μl capacity Hamilton liquid syringe may be used. It should be cleaned immediately after use by alternately drawing in and expelling methanol five to 10 times and then completely drying it by flowing dry nitrogen or pure air through the body of the syringe.

The calculated (see equation 11 above) amount of the liquid test compound is then injected into a 1-liter bulb, modified as shown in Figure 9, which has been preflushed with pure air into the hood for $\geq$ 5 minutes. The contents of the dosed 1-liter bulb are then flushed into Side A of the bag with pure air at a known flow rate, which should be ~3.5 liter min^{-1} for a more volatile liquid or less (~1-2 liter min^{-1}) for a non-volatile liquid. Evaporation of the lower volatility liquids may be aided by gentle use of a heat gun to warm the 1-liter bulb (taking care not to pyrolyze the test compound). The time and flow rate employed should be noted in flushing the test compound into Side A

4. Ozone Monitoring Prior to Mixing Sides A and B

While filling Side A, the O_3 monitoring instrument should begin sampling from Side B to establish a steady O_3 concentration prior to mixing Sides A and B. If the O_3 reading continually and rapidly falls, this

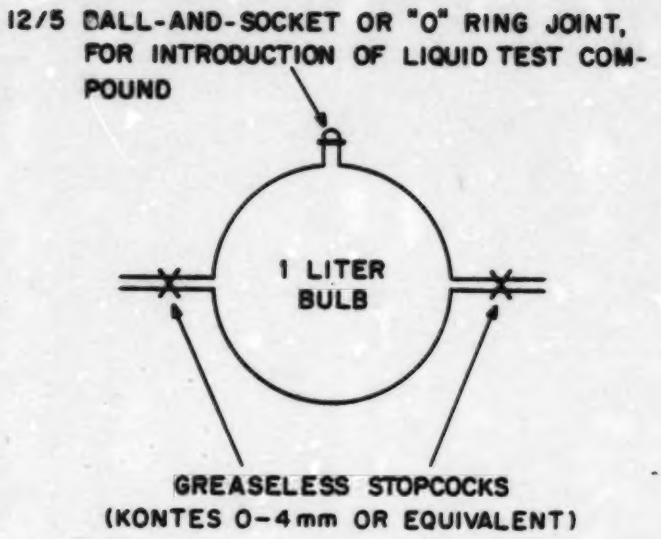

12/5 BALL-AND-SOCKET OR "O" RING JOINT, FOR INTRODUCTION OF LIQUID TEST COMPOUND
1 LITER BULB
GREASELESS STOPCOCKS
(KONTES 0-4 mm OR EQUIVALENT)

Figure 9. Design of Pyrex bulb for injection of liquid compounds.

indicates a significant leak across the metal rod barriers, and it may then be necessary to fold the bag around the rods more times or to tighten the clamps holding them in place.

The sampling rate of the O_3 analyzer should be known and the time period prior to t = 0 of sampling of air from Side B should be recorded. This allows the volume of air sampled from Side B prior to t = 0 to be calculated.

5. Barriers Removed at Time t = 0

After Side A has been filled, the test compound introduced, and the O_3 reading from Side B has stabilized, the barriers should be removed. Just prior to t = 0, the recorder should be set on a range such that after the O_3 in Side B is diluted with the contents of Side A the resulting O_3 concentration is > 50% of full scale. The entire reaction bag is mixed for 1 to 1.5 minutes and if a stripchart recorder is used continuous monitoring of the O_3 concentration is carried out as shown in Figure 10. If no stripchart recorder is available, the times and ozone concentrations at those times must be recorded manually.

The room temperature should be measured during each run using a thermometer.

The reaction should be monitored until ~0.100 ppm of O_3 is remaining, or for ~3 hours, whichever occurs first.

6. Data Analysis

The analysis of the data is similar to that used in determining the background O_3 loss rate, k_w.

a. Determination of O_3 Decay Rate. The O_3 concentrations should be first listed as a function of time. Ten data points should be obtained; if the reaction is fast, three half-lives only should be used, and the O_3 decay monitored over a factor of ~8 decrease from the initial concentration; if the reaction is slow then 10 equally spaced data points should be obtained, i.e., every 15-20 minutes. Values of $\ln([O_3]_{t_o}/[O_3]_t)$, where $[O_3]_{t_o}$ is taken to be the O_3 concentration after the mixing of the reaction bag is complete, are calculated at times $(t-t_o)$. Data points with O_3 concentrations below ~0.100 ppm should be excluded since the measurement uncertainties below this concentration can become significant.

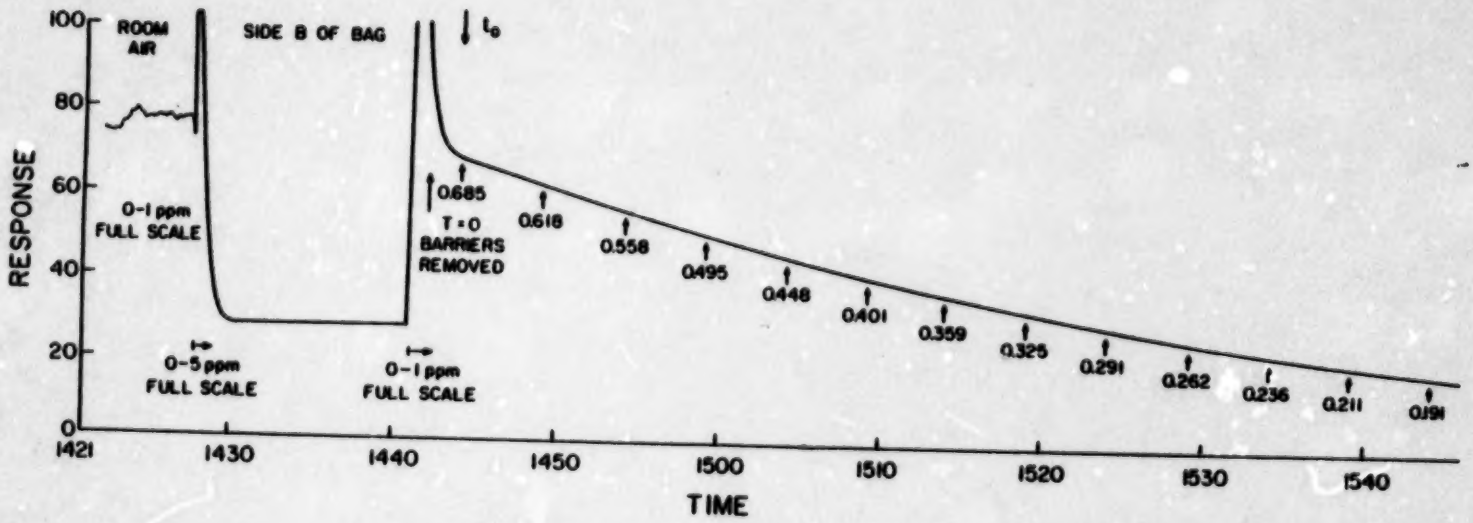


Figure 10. Ozone decay in the presence of a test compound, as monitored on a stripchart recorder.

The O_3 decay rate, $-d\ln[O_3]/dt$, is then obtained from a plot of $\ln([O_3]_{t_o}/[O_3]_t)$ against $(t-t_o)$, as shown in Figure 11. The slope is obtained by a least squares analys .

If the plot is curved, then the bag should be checked for leaks, the ozone monitor should be checked for linearity, and the determination of the ozone decay rate at that test compound concentration should be repeated.

b. Determination of Test Compound Concentration

The calculation of the organic concentration of the test compound requires that the volume of the entire reaction bag at time t = 0 be known. This is obtained from the volumes of Sides A and B at the completion of their pure air fills, minus the volume of air sampled from Side B prior to t = 0.

Knowing this volume, the concentration of the test compound in the reaction bag can be calculated, since, for gases,

$$\text{conc. (ppm)} = \frac{\text{ml of test compound injected} \times 1000}{\text{vol. of bag in liters}} \qquad (12)$$

and for liquids,

$$\text{conc. (ppm)} = \frac{\text{volume of test compound injected } (\mu l)}{\text{volume of bag (liters)} \times \text{molecular weight (g)}} \times \text{density of test compound } (g\ cm^{-3}) \times 24.6 \times 10^{-3} \qquad (13)$$

c. Calculation of O_3 Reaction Rate Constant

The above experiment and data analysis yields the ozone decay rate, $-d\ln[O_3]/dt$, at a given test compound concentration. If the ozone decay rate in the presence of the test compound is less than ~3 times the values of k_w obtained during the determination of the ozone reaction rate constants then, if allowed by its vapor pressure, the concentration of the test compound should be increased by a factor of 3. Values of the O_3 decay rate, $-d\ln[O_3]/dt$, should be determined for at least three different concentrations of the test compound (all sufficiently high such that the ozone decay rates are significantly, i.e., a factor of ~3-5, higher than k_w, if possible).

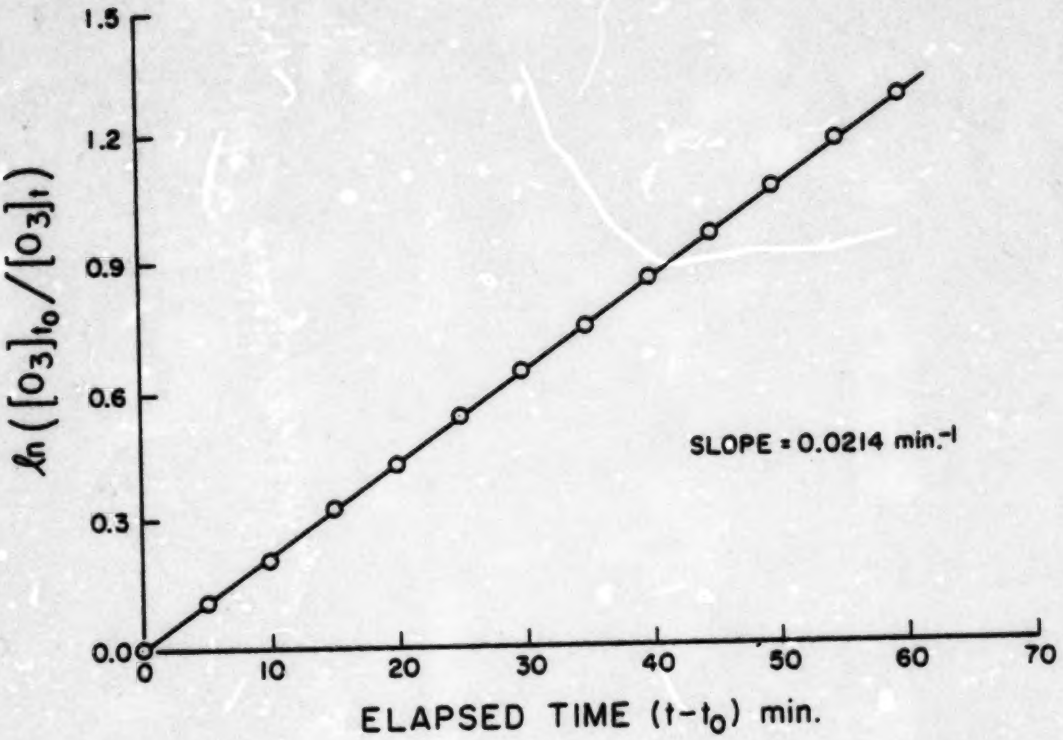


Figure 11. Plot of $\ln([O_3]_{t_o}/[O_3]_t)$ against $t-t_o$ for the data of Figure 10.

Then, as indicated by equation 6 a plot of $-d\ln[O_3]/dt$ against the concentration of the test compound should be a straight line with an intercept of k_w (experimentally determined) and a slope of k^{O_3}. Such a plot is shown for the case of o-cresol in Figure 12.

It is possible that at the highest test compound concentrations used (whether limited by vapor pressure or 100 ppm, whichever is lower) no significant increase in O_3 decay rate over the background value of k_w will be observed. This then leads to an upper limit for k^{O_3}. Thus if the increase in O_3 decay rate over the background is less than 0.01 min^{-1} (the maximum value of k_w recommended), then for 100 ppm of test compound, $k^{O_3} \leq 10^{-4}$ ppm^{-1} min^{-1} (7×10^{-20} cm^3 $molecule^{-1}$ sec^{-1}), which is of generally negligible importance under atmospheric conditions, as discussed in Section 1.

To convert k^{O_3} from ppm^{-1} min^{-1} units to cm^3 $molecule^{-1}$ sec^{-1} units, multiply by 2.27×10^{-18} x temperature (in degrees Kelvin).

7. Information to be Reported

A report of the results should include for each test compound the following:

a. The compounds name, formula and physical properties (boiling and melting points)

b. The chemical's physical form used during injection (gas or liquid at room temperature), method of purification and purity (including analysis of impurities)

c. The temperature during each run

d. The test compound concentrations and the ratios of [test compound]/$[O_3]_{initial}$

e. The plots of $\ln([O_3]_{t_o}/[O_3]_t)$ vs. time, and the slopes of the lines derived from such plots

f. The values of k_w determined during this experimental determination

g. A plot of O_3 decay rate (the slopes in [e]) against the test compound concentration, and the value of k^{O_3} determined, in ppm^{-1} min^{-1} and cm^{-3} $molecule^{-1}$ sec^{-1} units.

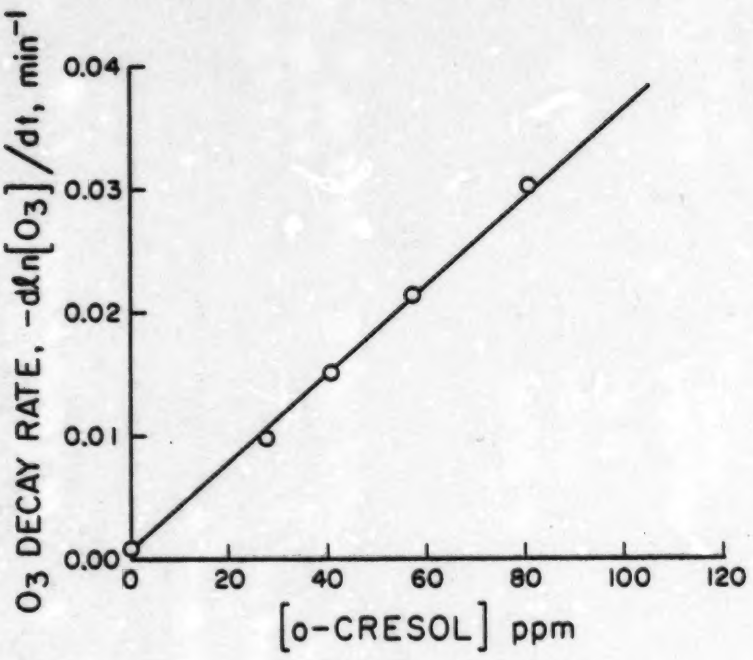


Figure 12. Plot of ozone decay rate against test compound concentration for the case of ortho-cresol.

h. Calculated 1/e lifetimes for (a) 40 ppb of O_3 and (b) 120 ppb of ozone, the latter being more representative of polluted urban conditions.

The Appendix gives a "checklist" for carrying out the above discussed procedures.

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APPENDIX

A. EXPERIMENTAL CHECKLIST

A. Equipment Needed

1. Calibrated ozone monitor
2. Ozone generator
3. 1-10 liter min^{-1} rotameter
4. Wet test meter or bubble flowmeter
5. All-glass gas syringes (5 and 100 ml) and microliter liquid syringes
6. Teflon reaction bag with sampling/injection ports
7. Metal bars
8. Strip chart recorder (if possible)
9. Stopwatch or timer
10. Opaque plastic sheet
11. Injection valves
12. 1/4" Swagelock caps and fittings
13. Purified and analyzed test compound

B. Calibration/Control Runs

1. Calibrate rotameter
2. Determine ozone generator output

C. Determination of k_w

1. Warm up O_3 monitor
2. Fill reaction bag with known amount of pure air
3. Cover reaction bag with opaque sheet
4. Inject requisite amount of O_3
5. Mix contents of bag
6. Commence ozone monitoring from bag. First 3-5 minutes of data should not to be used in the data analysis.

D. Determination of O_3 Reaction Rate Constants k^{O_3}

1. Warm up O_3 monitor
2. Divide reaction bag
3. Fill side B with known amount of pure air

4. Inject requisite amount of O_3 into side B
5. Commence ozone monitoring from side B
6. If test compound is gaseous, fill side A with known volume of air and introduce requisite volume of test compound. If test compound is liquid, flush requisite amount of test compound into side A from bulb and fill side A with known volume of air.
7. Check O_3 concentration in side B—is it constant with time and of the correct magnitude? If not, check for leakage across barriers or adjust concentration accordingly.
8. Remove barriers, note time of O_3 sampling from side B.
9. Mix contents of reaction bag for 1-2 minutes.
10. Monitor O_3 concentration until O_3 concentration decreases by a factor of 10 or for 3 hours, whichever comes first.
11. Analyze data